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IGNITION DELAY OF TRIETHYL TRITHIOPHOSPHITE WITH NITRIC ACID

Contract N7 onr-462
Task Order III
Item 10

17 February 1953

Report No. 680
(Final)

A STUDY OF THE IGNITION DELAY OF TRIETHYL TRITHIOPHOSPHITE WITH NITRIC ACID IN AN IMPINGING-STREAM ROCKET STARTER MOTOR

Contract N7onr-462
Task Order III
Item 10

Written by:

E. M. Wilson

No. of Pages: 16

Approved by: S. B. Kilner
S. B. Kilner
Asst. Senior Chemist
Solid Engine and
Chemical Division

Period Covered:

11 November 1952 through 11 January 1953

Approved by: D. L. Armstrong
D. L. Armstrong
Principal Chemist
Solid Engine and
Chemical Division

AEROJET ENGINEERING CORPORATION

Azusa, California

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CONTRACT FULFILLMENT STATEMENT

This final report completes the fulfillment of Item 10, Amendment 7 to Contract N7onr-462, Task Order III.

Report No. 680

I. OBJECTIVE

The work described herein was authorized by Amendment 7, Item 10, to Contract N7onr-462, Task Order III, which required an investigation of the ignition delay of triethyl trithiophosphite with specially adjusted nitric acid. Delays were to be measured in a small rocket motor at temperatures of 70, 32, and -40°F, with fuel containing 0, 10, 20, 30, and 40 vol% n-heptane. The nitric acid used in the study was to be adjusted to 1.0% water, 0.5% nitrogen dioxide, and 98.5% nitric acid.

II. RESUME

A. PROBLEM

Several contractors have developed laboratory-scale testers for the determination of the delay of spontaneous ignition of rocket fuels with nitric acid (e.g., cf. References 1 and 2). In order to compare results obtained from such equipment with the delays that would actually occur in rocket motors, it is necessary to determine the delays in the various apparatus and in small rocket motors with identical propellants. A program was therefore organized by the Bureau of Aeronautics with this aim in mind. The propellants selected for this study, and furnished to each contractor, were triethyl trithiophosphite, n-heptane, and highly purified nitric acid, the latter to be adjusted to agreed-upon percentages of water and nitrogen dioxide. Each contractor was then to measure the delays in his own tester so that a comparison of the results could be made.

B. TEST RESULTS

1. A small rocket motor using a single pair of impinging fuel and oxidizer streams, and equipped with a photocell and a pressure pickup, was used for the 55 tests performed during this program. Complete data are given in Section V of this report. Numerous hard starts were obtained with the diluted fuel mixtures, the combustion being so rapid after ignition that excessive pressures resulted. The high pressures caused damage to the photocell assembly or pressure pickup, although only in the last run (with 70% triethyl trithiophosphite and at ambient temperature) was the motor itself damaged.

2. It was possible to obtain reliable values of ignition delay for the 100% and 90% triethyl trithiophosphite. However, many of the tests with the 80% mixture, and all with the 70% mixture, gave hard starts and long, variable ignition delays. As a result, it was considered pointless to continue the tests into the lowest range of triethyl trithiophosphite concentration.

3. The ignition-delay values show no dependence upon concentration or temperature with 100% and 90% triethyl trithiophosphite. The values with more dilute fuel mixtures were so variable that it is not possible to establish any trend.

4. The use of both photocell and chamber-pressure pickup allowed comparison of the time of ignition indicated by these two methods. In all cases in which both were used, the time of ignition was the same by both methods, to within the precision of measurement (0.5 millisec).

5. The reaction of personnel to exposure to vapors of triethyl trithiophosphite indicated that precautions similar to those prescribed for aniline or hydrazine are necessary in handling this material. However, because of the immediate nausea resulting from exposure to small amounts of the material, the dangers of systemic poisoning are thought to be less than with toxic agents having a more subtle effect.

III. CONCLUSIONS AND RECOMMENDATIONS

A. It was the primary aim of this work to obtain test data on ignition delay in equipment that duplicated actual rocket motor conditions, for comparison with the results on identical propellants in laboratory testers. This aim has been achieved by determining the composition and temperature ranges over which satisfactory motor ignition could be obtained. The test motor was designed to duplicate as closely as possible the starter motors actually in use, which have been evolved in attempts to make the ignition of a rocket motor reliable under a wide variety of conditions. Thus it is seen that with 100% and 90% triethyl trithiophosphite, over the range of temperatures studied, the ignition delay was short and almost constant. On the other hand, the more dilute mixtures gave the long, variable ignition delays and hard starts that have caused trouble in the past in the design of starting mechanisms and in the selection of propellants for rocket motors.

B. This study indicates that triethyl trithiophosphite exhibits sufficiently short ignition delays at low temperatures to be considered for use as a rocket fuel in cases where hypergolicity is an important factor. The fuel is known, however, to be sensitive to air oxidation and gum formation, and it is thought that in the small-scale tests reported herein, some but not all of the variability was caused by small amounts of air oxidation, well below the level that results in gum formation. At least one other contractor (Reference 3) has recorded variable results with this fuel.

C. It is recommended that further work be done on the correlation of laboratory and test-engine ignition delays, with propellant combinations that are less sensitive to handling techniques.

IV. TESTING METHODS

A. PROPELLANTS

1. The nitric acid used in this program was manufactured by the General Chemical Division of the Allied Chemical & Dye Corporation, and was shipped as the frozen solid in as anhydrous a condition as possible. The acid was analyzed and adjusted as nearly as possible to the specifications given in

Paragraph I. The adjusted acid was found to contain 98.31% HNO_3, 1.09% H_2O (by Karl Fischer titration), 0.56% NO_2, and 0.04% solids. The 4-lb lot of acid was divided among 10 bottles, which were stored at -80°C until used.

2. The triethyl trithiophosphite was prepared by the California Research Corp., and was furnished in four sealed 0.5-lb glass ampoules. The material received at Aerojet was Serial No. 53070-R, Batch No. 1.

3. The ASTM n-heptane was supplied by the Phillips Petroleum Co.; it was taken from Lot No. 297.

B. IGNITION-DELAY TESTER

1. The ignition delays were measured in a small motor assembled from standard rocket starter-motor parts, except that the motor chamber consisted of a 1-1/4-in. aluminum alloy elbow (AN833-20D). This arrangement permitted the use of a photocell to record the instant of ignition by the first production of flame. Except for the unusual shape of the chamber, the apparatus was as nearly as possible a duplicate of a standard starter motor. The assembly and details of the apparatus are shown in Figure 1, and three general views in Figure 2. A schematic diagram of the entire system is shown in Figure 3.

2. Six openings were present in the tester:

a. A removable sonic nozzle, 0.205 in. in diameter, was attached to one end of the elbow.

b. A Pyrex window was sealed onto the vertical portion of the elbow. A photocell was placed above this window for observing the time of first appearance of visible reaction.

c. A 1/4-in. fitting in the side of the elbow was connected by 2 in. of 1/4-in. tubing to a pressure pickup. Electronic Bourdon-type and diaphragm reluctance gages were used.

d. Another 1/4-in. fitting in the opposite side of the elbow was connected with a pressure switch. This switch was used to close the propellant valve if a preset chamber pressure was not reached before a preset interval after the start of the test.

e. A 1/8-in. fitting with an 0.039-in. opening was used for introducing the nitric acid into the chamber.

f. Another fitting, with an 0.024-in. hole, was used for directing the fuel against the oxidizer stream. The included angle of the streams was 45°. (Note that Figure 1 shows a different size; the orifice was changed to the above value before calibration.)

3. The tester had a volume of 77 cc, giving it an L^* of 142 in. At the propellant flows used, a chamber pressure of approximately 250 psia was maintained after ignition.

4. The propellant tanks consisted of approximately 16 in. of 3/8-in. aluminum tubing, having a volume of approximately 30 cc each. Nitrogen pressurization was used for the displacement of the propellants, the mixture ratio being controlled by the pressures applied to the separate lines. The storage lines were connected to a standard Aerojet starter valve, in which oxidizer and fuel pintles are yoked together. This valve was actuated by nitrogen supplied by the opening of a solenoid-operated Saval valve. The propellant valve was equipped with a valve-motion indicator on the yoke, giving a record of valve position on the oscillograph. Approximately 4 in. of 1/8-in. stainless steel tubing led from each side of the propellant valve to the ends of the injectors. The valve was set to give a slight acid lead (about 0.1 millisec).

5. Nitric acid was added to the storage line by removing the cap on a cross in the line and filling it from a fresh bottle of acid. The propellant valve was briefly opened to bleed the acid down through the valve. Triethyl trithiophosphite was added through a cross in the fuel line. It was removed by means of a hypodermic syringe from bottles equipped with rubber serum stoppers in order to reduce the exposure to air to a minimum. The fuel was then bled through to the valve.

C. TESTING

1. All tests were controlled by an electrical sequencing unit. This equipment was normally set to terminate the run if the chamber pressure had not reached 60 psig by 0.10 sec from the time of initiation of the test. At the risk of seriously damaging the equipment, the propellant valve was kept open for 0.25 sec in some cases where ignition appeared to be difficult.

2. Signals from the valve-motion indicator, photocell, and pressure pickup were recorded on a multichannel oscillograph. A typical record is shown as Figure 4. The vertical time traces are 10 millisec apart. "LSV," "Photocell," and "P_{cs}" indicate, respectively, valve position, photocell response, and chamber pressure. Ignition delays were determined from these records by measuring the time interval from the first slow rise in chamber pressure to the point of the first very rapid increase. The photocell trace was used to verify the results obtained by the pressure-rise method. In no case in which both were used was there any perceptible difference between the ignition times by the two methods. Preliminary runs with an open-circuit probe at the impingement point and with commercial WFNA in the propellant lines showed that the time from initial valve motion to impingement averaged 5 millisec. During the testing with the pure propellants it was found that, although the average point of initial pressure rise approximated this calibration, there was a variation of several milliseconds from one test to the next. It was therefore decided that the time of impingement would be taken as the point of the first pressure rise, and not the predetermined factor obtained when the probe was in the motor.

3. The entire testing unit, including the sections of tubing which contained the fuel and oxidizer, was placed in a bath of circulating trichloroethylene. This bath was cooled with dry ice for the low-temperature tests.

V. SUMMARY OF RESULTS

A. The ignition-delay values in millisec are given in Table I. The firings with 100% trithiophosphite show no perceptible trend with temperature. It may well be that a preignition reaction of the fuel and oxidizer mixture in the motor chamber warms up a portion of the reactants enough to obscure the effects of changing temperature of motor walls and bulk propellants. When the trithiophosphite is diluted with n-heptane to 90%, no change in ignition delay either with concentration or temperature is noted. At 80% and below, difficulties with long delays and hard starts were encountered, and reproducibility was very poor. No firings were made at 60%, since the last run at 70% (No. 89) distorted the motor so that the propellant streams no longer impinged. It is apparent that no trend either with temperature or with fuel composition has been established, although it is certain that hard starts and variable performance result from dilution of the hypergolic fuel with a non-hypergolic diluent. This tendency was confirmed independently by the results obtained under a separate program in which a standard motor was employed in tests of mixed alkyl thiophosphite mixtures with JP-4, burned with AN specification WFNA.

B. After every three to four tests the motor was serviced by cleaning it with solvent and blowing it dry with nitrogen. No correlation between test results and servicing of the motor was noted. Just before the last test, the motor was cleaned in hot WFNA, rinsed with water, and blown dry.

C. During the checkout of the equipment, eleven firings were made with mixed alkyl thiophosphites, four with the hydrocarbon fuel HF-D, and one with 65% aniline and 35% furfuryl alcohol, all with AN specification WFNA as oxidizer. The results of these tests are given in Table II. Results with the HF-D are noteworthy, inasmuch as this material is under consideration primarily because of its hypergolic properties. The ignition delay for the one test with the aniline and furfuryl alcohol mixture and WFNA was approximately 1.5 times that obtained for the same mixture with RFNA (Reference 2, Figure 25) in the larger, vertical test engine used by the Jet Propulsion Laboratory.

REFERENCES

1. Progress Reports No. 5 and 6, Contract NOrd 11338, Phillips Petroleum Co. (Confidential).

2. D. M. Griffin, Progress Report No. 9-30, Jet Propulsion Laboratory, California Institute of Technology, 17 May 1949 (Confidential).

3. Progress Report No. 8, Contract NOrd 11338, Phillips Petroleum Co., October 1952 (Confidential).

TABLE I

IGNITION-DELAY VALUES

Test No.	Vol% $(C_2H_5S)_3P$	Vol% n-Heptane	Temp °F	Ignition Delay millisec	Remarks
34	100	0	75	6	
35	100	0	75	7	
36	100	0	75	7	
37	100	0	60	46	
38	100	0	60	19	Flameout after ignition
39	100	0	60	11	
40	100	0	60	5	
					Mean value, 6 millisec, neglecting Tests No. 37, 38, and 39.
41	100	0	28	5	
42	100	0	30	6	
43	100	0	28	6	
					Mean value, 6 millisec
44	100	0	-38	5	
45	100	0	-39	6	
46	100	0	-41	5	
					Mean value, 5 millisec
51	90	10	80	6	P_c pickup damaged
62	90	10	77	6	
63	90	10	77	6	
64	90	10	76	5	
52	90	10	60	6	No photocell
53	90	10	60	5	No photocell
54	90	10	60	5	No photocell
55	90	10	60	6	No photocell
					Mean value, 6 millisec
56	90	10	24	6	
57	90	10	24	6	
58	90	10	25	7	
					Mean value, 6 millisec
59	90	10	-38	4	
60	90	10	-38	6	
61	90	10	-38	5	
					Mean value, 5 millisec
48	80	20	70	185	Photocell destroyed and 1500-psi pickup damaged
49	80	20	70	79	1500-psi pickup damaged; no photocell
50	80	20	70	68	3000-psi pickup damaged; no photocell

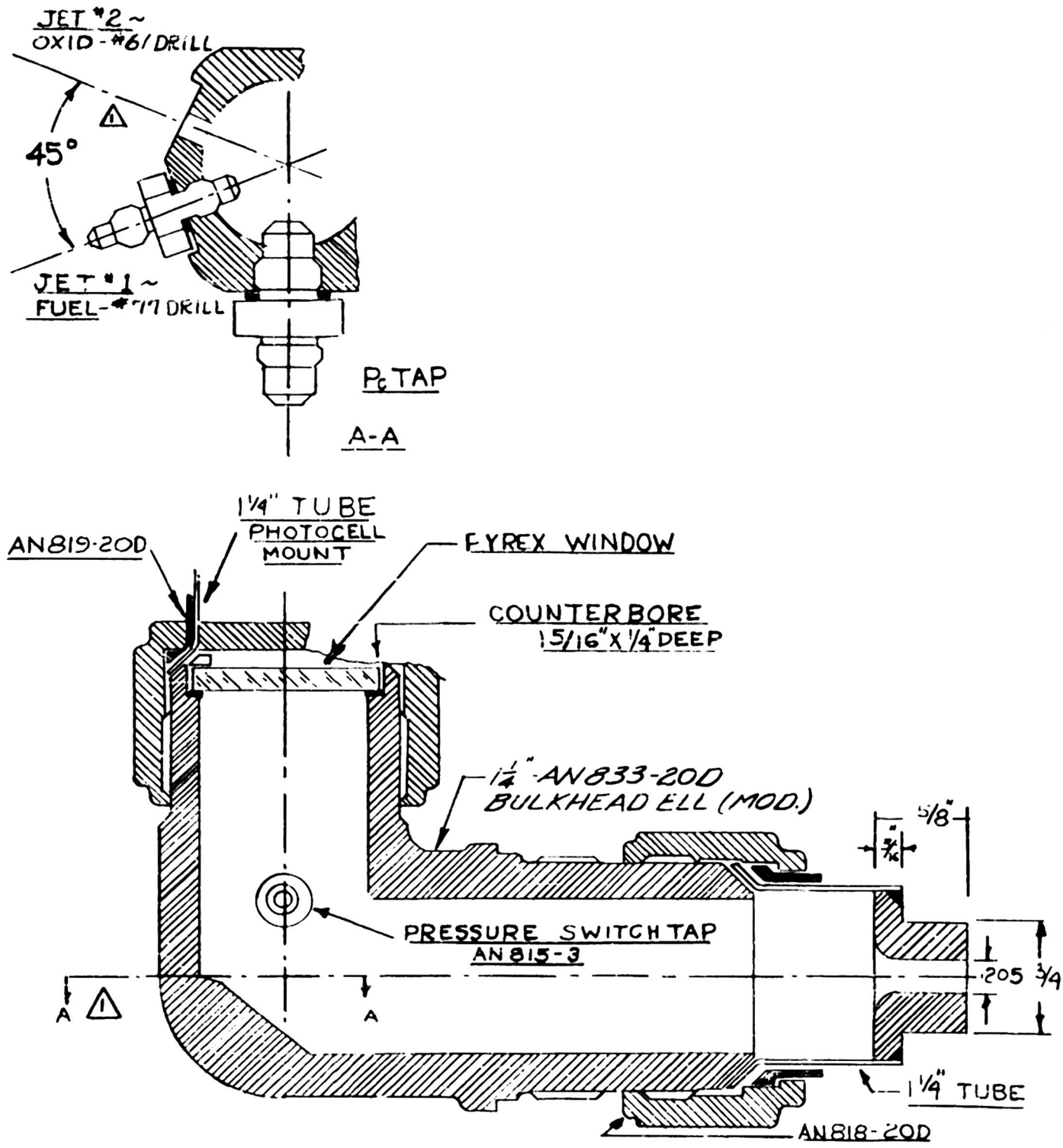
TABLE I (cont.)

Test No.	Vol% $(C_2H_5S)_3P$	Vol% n-Heptane	Temp °F	Ignition Delay millisec	Remarks
65	80	20	60	>160	Malfunction control terminated run before ignition
66	80	20	60	215	3000-psi pickup damaged; no photocell
67	80	20	64	8	Different fuel mixture from that used above because of possible exposure of other fuel to air; no photocell
68	80	20	64	8	No photocell
69	80	20	64	7	No photocell
70	80	20	65	14	No photocell
74	80	20	60	113	No photocell; new fuel mixture because of hard starts on Runs 72 and 73
75	80	20	60	74	No photocell
76	80	20	60	47	No photocell
77	80	20	60	11	No photocell
78	80	20	30	19	No photocell
79	80	20	31	19	No photocell
80	80	20	32	18	No photocell
71	80	20	-42	8	No photocell
72	80	20	-40	52	Pickup damaged
73	80	20	-40	94	Pickup damaged; photocell destroyed
85	70	30	60	175	No photocell; pickup damaged
86	70	30	60	219	No photocell; pickup damaged
87	70	30	60	213	No photocell; pickup damaged
89	70	30	70	ca. 71	No pickup on; delay obtained by subtracting 5 millisec from time of valve opening to photocell trace rise before it was destroyed; motor had been cleaned in hot WFNA and impingment checked beforehand
88	70	30	-38	99	No photocell; reluctance pickup seriously damaged and cap on vertical arm bulged
	60	40			No tests made

TABLE II

IGNITION TESTS WITH OTHER FUELS

Run No.	Fuel	Ignition Delay, millisec	Temp, °F
23	Crude mixed alkyl thiophosphites	12	70
24	↓	11	70
25		9	70
26		No ignition	-40
27		18	-40
28		62 (Poor run, low chamber pressure)	-40
29		No ignition	-40
30		No ignition	65
31		No ignition	65
32		11 (new fuel and oxidizer)	60
33	↓	12	-40
22	65% aniline - 35% furfuryl alcohol	42	70
18	HF-D	No ignition	70
19	↓	↓	70
20			70
21	↓	↓	70



⚠ OXIDIZER JET NOT SHOWN

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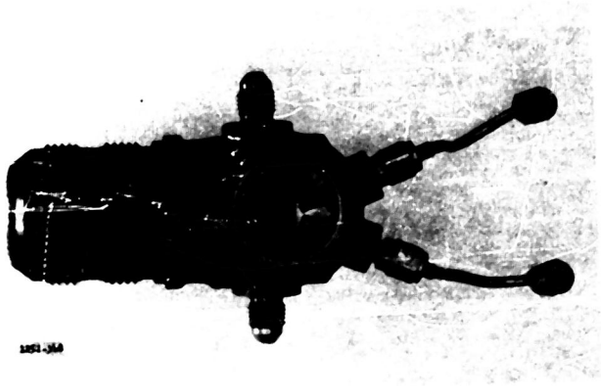
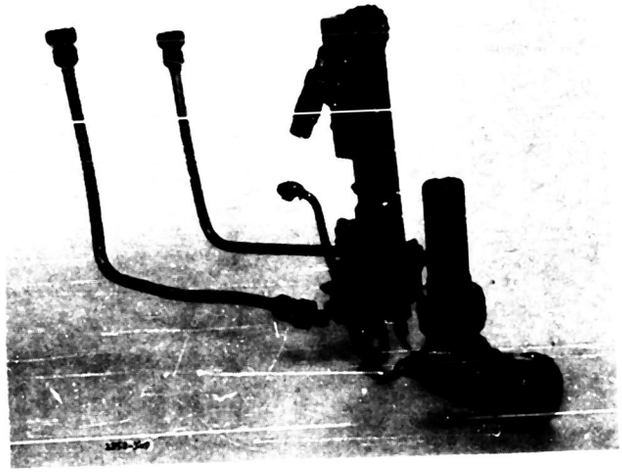
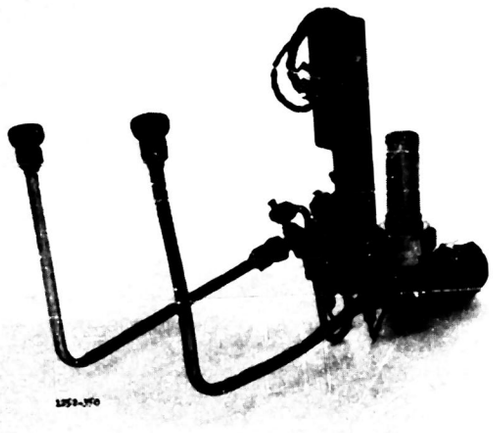
Assembly and Details of Impinging-Stream Ignition-Delay Tester

Figure 1

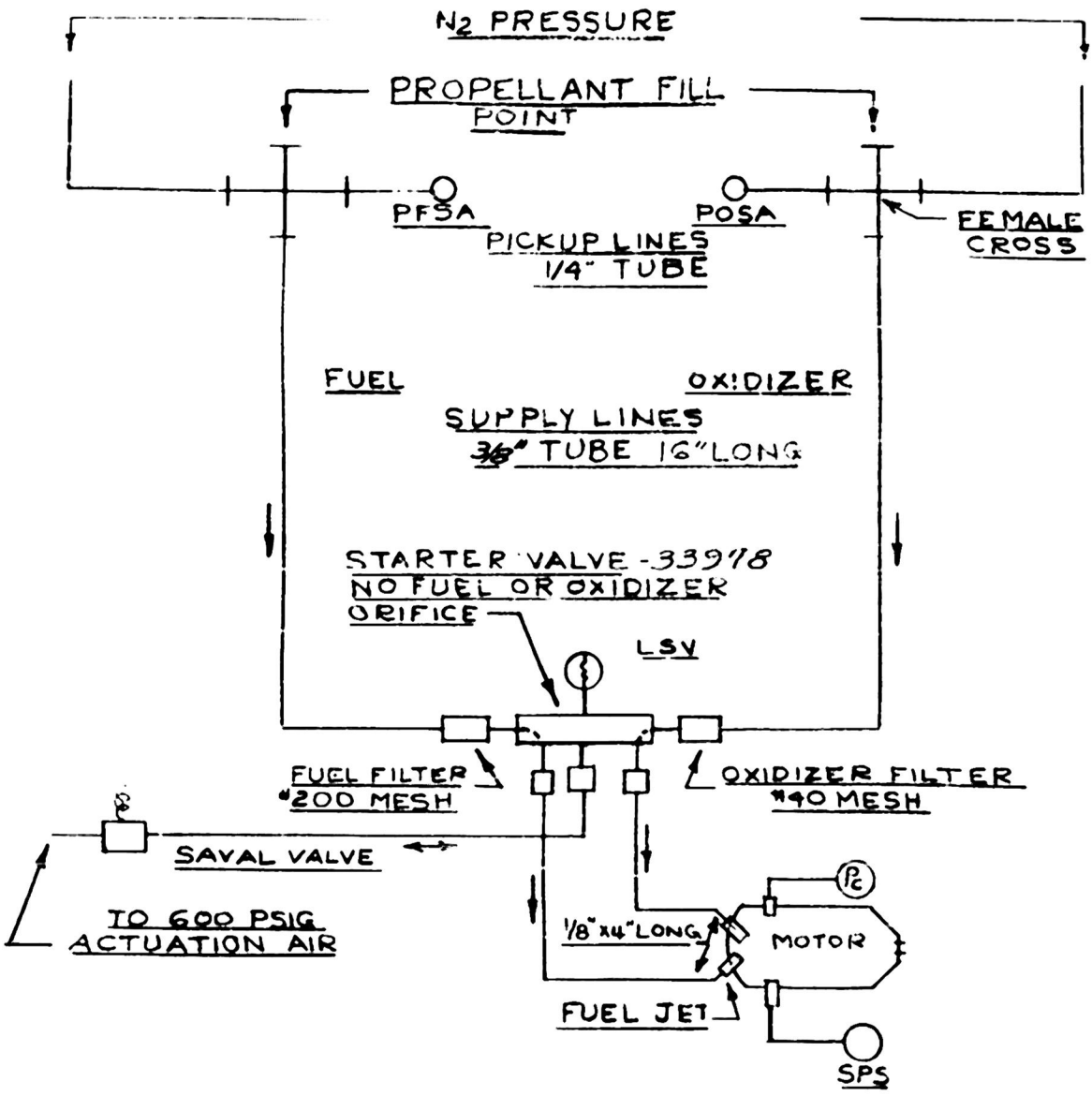






General Views of Ignition-Delay Tester

Figure 2



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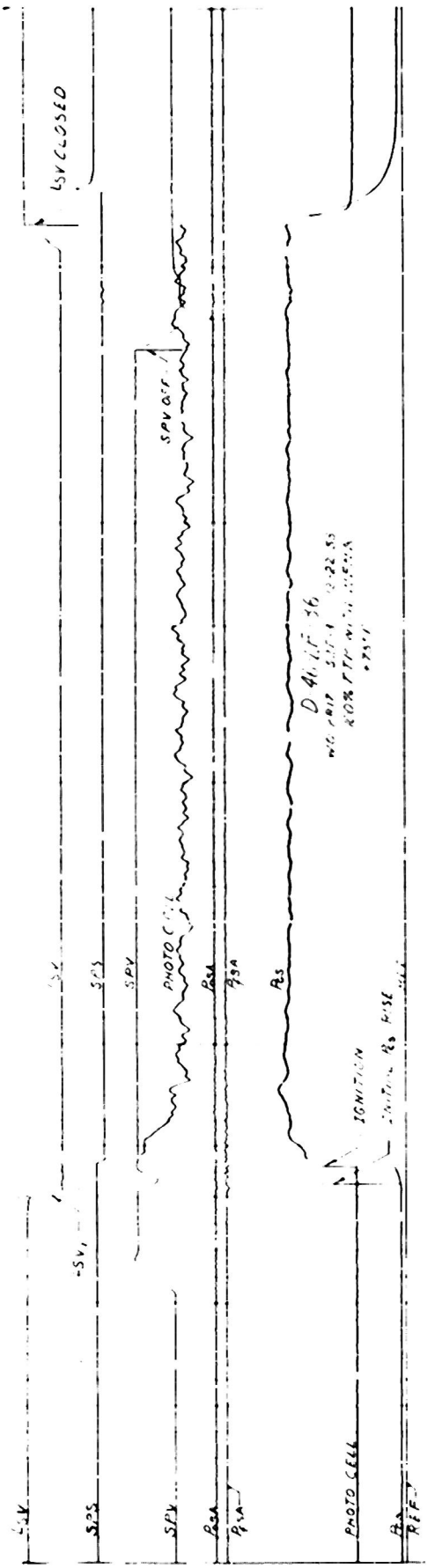
Schematic of Ignition-Delay Tester and Associated System

Figure 3



Typical Oscillograph Record of Ignition-Delay Test

Figure 1